

**WHAT'S SO SPECIAL ABOUT  
ULTRANANOCRYSTALLINE DIAMOND?\***

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The excitement in the developing field of nanoscience and nanotechnology is partly a result of the startling changes in mechanical, electrical, and optical properties encountered in many materials when they approach single-digit nanometer dimensions. Frequently these changes can be traced in large measure to the fact that a substantial fraction (perhaps 10% or more) of the atoms in a nanocrystallite are on surfaces or, in the case of films, at grain boundaries. Diamond provides a particularly dramatic example of changes in properties because the  $sp^3$  and  $sp^2$  bonding configurations of carbon are so very close in energy ( $\sim 0.02$  eV). As a consequence, carbon atoms at the high-angle, high-energy twist grain boundaries of ultrananocrystalline diamond (UNCD) films are able to lower their free energy by rehybridization rather than by bond bending. The implications of this unique situation are of special interest because the complex bonding situation at the grain boundaries introduces a plethora of states into the band gap providing rich opportunities for tuning the electronic properties of diamond while improving the fracture strength and tribological properties of the material.

We have discovered that at very low hydrogen contents, carbon containing argon microwave plasmas give rise to a new growth and nucleation species, carbon dimer,  $C_2$ . Very high heterogeneous renucleation rates ( $\sim 10^{10}$   $cm^{-2}$   $sec^{-1}$ ) result in films composed of randomly oriented crystallites with dimensions of 3-5 nanometers. This is in contradistinction to conventional CVD diamond films grown in the presence of large amounts of hydrogen resulting in micron size crystallites.

Since one cannot change either the composition or the molecular structure of diamond, manipulating the microstructure remains the only alternative for tailoring properties in such a way as to be able to take maximum advantage of diamond's many outstanding characteristics. UNCD thus has turned out to be an important exemplar of the drastic changes in materials properties that can be occasioned solely by the reduction in crystallite size to the nanoscale which in turn lead to a greatly extended range of applications.

The carbon dimer growth species, unlike either the methyl radical or acetylene growth species involved in microcrystalline CVD diamond synthesis, can insert directly into carbon-carbon and surface carbon-hydrogen bonds without the intervention of atomic hydrogen. Extensive quantum chemical calculations that model the (110) and (100) surfaces have been performed to understand the  $C_2$  growth mechanism. The calculations give a theoretical value of the activation energy for UNCD growth of 5 Kcal/mol, much less than the value 24 Kcal/mol calculated for microcrystalline diamond growth. Our most recent experimental value for  $C_2$  growth is 4 Kcal/mol leading to growth near 350°C of highly dense, phase pure UNCD at rates of 0.1  $\mu m/hr$  which is higher by 2-3 orders of magnitude compared to microcrystalline diamond growth rates at this temperature. Remarkably, we have demonstrated coating UNCD onto silicon wafers

carrying C-MOS circuitry while maintaining a functioning electronics package after deposition.

Procedures have been elaborated by us to fabricate complex UNCD MEMS devices using standard lithographic masking procedures and deep reactive oxygen ion etching. Potentially it will be possible to take advantage of diamond's high Young's modulus coupled with UNCD's high fracture strength to realize the long hoped for goal of RF MEMS integrated with standard silicon chip technology.

Nitrogen doped UNCD has shown itself to be a versatile electrochemical electrode with a 4eV "window" in aqueous solutions displaying good kinetics in several test redox systems studied in collaboration with Prof. Greg Swain, Michigan State University. In very recent work done in collaboration with Prof. Robert Hamers, University of Wisconsin, UNCD surfaces, functionalized with DNA, have shown no degradation after dozens of hybridization-dehybridization cycles. This work has been extended to protein functionalization and is clearly relevant to the development of a wide range of biosensors and bioactuators such as nerve stimulating electrodes.

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